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An Investigation of Kundt's Rule.

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AN INVESTIGATION OF KUNDT'S RULE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Charles Edward Reid
B.E., Tulane University, 1939
M.S., Louisiana State University, 1947
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ABSTRACT

In 1874 August Kundt stated that if a given colored compound is dissolved in several solvents, the absorption bands will be shifted toward greater wave-length the higher the dispersion of the solvent. In much of the work on Kundt's rule the refractive index has been taken to be the criterion instead of the dispersion. Although the rule (in either form) has been supported or denied by various investigators, a systematic attempt to determine the conditions in which it applies has been lacking. In particular, the important effect of solvation in shifting the absorption bands to greater wave-length (the Kuhn-Brockmann effect) has been widely ignored.

The present work was undertaken in order to determine the conditions in which Kundt's rule is valid and to provide a reasonable interpretation of the underlying physical phenomena. Further incentive was found in the hope that the results might be useful in spectrophotometry and in investigations of chemical constitution.

The experimental method consisted in making up solutions of colored compounds of selected chemical types in

a wide variety of solvents and determining the absorption spectra by means of a Beckmann spectrophotometer.

Kundt's rule, in either form, has been found to hold for systems consisting of a solute having a zwitter ion among its important resonating forms dissolved in a hydrocarbon or aryl halide. If in the solvent the polarizability of one bond is greater than the average polarizability of the whole molecule, the spectrum is shifted farther toward the red end than it would be in a hydrocarbon solvent of the same refractive index. This effect is larger if the solute has highly polar bonds. If solvation occurs, a large Kuhn-Brockmann effect is to be expected.

Brooker and Sprague asserted that solutes having a zwitter ion among their resonating forms absorb at greater wave-lengths in solvents of higher dielectric constant, and offered as explanation that the Coulombic energy of the zwitter ion form is reduced by the dielectric properties of the solvent. In the present work it has been found necessary to modify this interpretation by the assumption that only that portion of the dielectric constant which is due to electronic polarizability is operative in the small region near the solute molecule. The close relation of electronic polarizability to refractive index then accounts for the empirical correlation of the position of the absorption bands with refractive index. If one part of the solvent molecule is more polarizable than the rest, an alignment in

which the molecules immediately surrounding the solute molecule turn their more polarizable parts toward the latter will further reduce the Coulombic energy; the reduction in energy will provide a driving force for the alignment and will also cause the extra shift toward greater wavelength noted in such solvents.

The position of the absorption maximum of phenol blue in hydrocarbon or aryl halide solvents can be correlated with the refractive index of the solvent by any of several empirical equations, of which the following is an example:

$$\nu_m = 441 + \frac{98.9}{n^2 - 0.997}$$

(n is refractive index, ν_m frequency at absorption maximum in fresnels.)

Iodine, phenolphthalein, and p-rosaniline, taken as representatives of halogens, anionic dyes, and cationic dyes respectively, do not follow Kundt's rule.

Voigt's attempt to treat Kundt's rule on the basis of classical electromagnetic theory is not applicable to systems in which the solute is an intricate organic molecule, since the fundamental postulate of this treatment - that the solvent does not affect the force constants within the solute molecules - does not hold.

INTRODUCTION

Observations that the absorption spectra of colored compounds in solution undergo slight displacements with change of solvent have led to several attempts to find some correlation between these shifts and the properties of the compounds involved. Kraus, for example, stated that the absorption bands of chlorophyll were shifted to longer wave-lengths the greater the specific gravity of the solvent (13). August Kundt, denying the validity of this rule, proposed the following relationship:

Mischt man zu einer absorbirenden Substanz andere nicht absorbirende Medien, so rückt ein Absorptionsstreifen, welcher sich im Bereiche λ_1 bis λ_2 des Spectrums befindet, um so weiter nach dem rothen Ende des Spectrums, je grösser die Constante B der Dispersionsformel $n = A - B/\lambda^2$ ist, welche in dem Bereich λ_1 bis λ_2 die Dispersion des zugesetzten nicht absorbirenden Mediums darstellt (16).

Later (15) he published an account of the experiments on which the rule was based. Although Kundt, as the above quotation shows, considered the dispersion of the solvent to be the controlling factor, the term "Kundt's rule" is often applied to the assertion that the shift is determined

by the refractive index of the solvent, larger shifts toward the red occurring in solvents of higher refractive index (22).

Voigt, utilizing classical electromagnetic theory and proceeding from the assumption that electrons acting as damped harmonic oscillators are responsible for the absorption of light, derived a relationship which he believed was the basis of Kundt's rule (25). According to this theory, the maximum absorption should lie where

$$\frac{\partial}{\partial \theta} \log_e (n_s^2 k_s) = \frac{\partial}{\partial \theta} \log_e n_o$$

In this formula θ is the reciprocal of the frequency, n the refractive index, and k the extinction coefficient. The subscript s refers to the solute and o to the solvent. Voigt made no attempt to correlate his theory with experimental data.

Knoblauch (11) has also given a mathematical treatment, according to which the wave-length at the absorption maximum should be directly proportional to the refractive index of the solvent. This treatment involves the relationship that the dielectric constant is equal to the square of the refractive index, and it can therefore be applicable, if at all, only to solvents having no dipole moment.

Vaillant (24) suggested the use of an equation of the form $\lambda = an - bd + c$, in which λ is the wave-length at the absorption maximum, n the refractive index, d the density of the solvent, and the other quantities experimental constants.

Recent support of Kundt's rule (in the refractive index form) has come from Sheppard (22). Without presenting any data, he stated that his investigations had shown the rule to be valid for a large class of dyes, provided "polar solvents" are avoided. In some cases he found a linear relationship between refractive index and wavelength and was able to find the position of the absorption maximum in vacuo by extrapolation of this relationship to a refractive index of unity.

Unpublished results of LeRosen on the spectra of carotenoids have also followed Kundt's rule. In this case the relationship is apparently not quite linear.

On the other hand, statements denying Kundt's rule have also been published. Brode (4) bases his denial on a study of phenyl azophenol; Mackinney (18)(19) uses the observation that chlorophyll has the same absorption maximum in acetone and dichloroethane. Houston (9) states that as many data can be found contradicting the rule as supporting it. According to Brooker and Sprague (5) the position of the absorption bands of the dye phenol blue is dependent on the dielectric constant of the solvent. This statement was based on the behaviour of phenol blue in only four solvents. Cennamo (7) reported that iodine solutions have spectra which are dependent on the dipole moment of the solvent, solvents of zero dipole moment giving identical spectra, while the spectra in solvents having a dipole

moment different from zero are unpredictable. Piccard's work (21), however, contradicts that of Cennamo.

Fortunately, most of the confusion resulting from these incompatible assertions can be resolved by an observation of Kuhn and Brockmann (14). These authors found that the absorption maximum of rhodoxanthin is shifted to longer wave-length by solvents which cause solvation. If this phenomenon occurs with other compounds also, it is sufficient to account for the divergences from Kundt's rule found by Brode, Mackinney, and Brooker and Sprague. For example, Brode uses a solute containing a hydroxyl group. If this solute is dissolved in a solvent containing an oxygen, nitrogen, or perhaps fluorine atom, solvation by hydrogen bonding is inevitable, and the absorption maxima in such cases should appear at longer wave-lengths than would otherwise be expected. Re-examination of Brode's data with these ideas in mind leads to good agreement with both Kundt's rule and the Kuhn-Brockmann rule. It is of interest to note that Kundt made up his solutions by adding one or two milliliters of a solution of the solute in alcohol or chloroform to the solvent to be tested (15). The purpose of this was to ensure equal concentrations in all solutions, but, since both alcohol and chloroform form hydrogen bonds with compounds containing oxygen and nitrogen, the result was that Kundt unwittingly circumvented the effect of solvation by using only solvated solutes in all cases.

These conflicting reports leave unanswered the question of the conditions, if any, in which Kundt's rule is valid. Furthermore, if the rule has any validity, a satisfactory interpretation of the physical phenomena involved is needed, since the modern theory of light absorption by organic molecules is quite different from that used by Voigt. Recent advances in the theory of color, based on the application of the resonance concept (3)(17)(26), should provide the foundations for such an interpretation. The present work was undertaken largely to answer these questions. Further incentive was found in the hope that a quantitative study of the effect might lead to results of value in settling questions of chemical constitution. Finally, a reliable method of predicting the effect of solvent on absorption spectra should be useful in the field of spectrophotometry.

EXPERIMENTAL WORK

The general plan of the experimental procedure in this work was to select colored compounds of several chemical types, dissolve them in various solvents, and determine the wave-length at which maximum absorption of light occurs. The colored compounds used as solutes included a halogen, an anionic dye, a cationic dye, and several non-ionic compounds. Among the solvents were hydrocarbons, halogen derivatives of hydrocarbons, alcohols, ketones, acids, ethers, carbon disulfide, pyridine, water, and aqueous solutions of glucose.

Measurements of absorption were made on a Beckmann photoelectric spectrophotometer. The concentration was such as to produce an extinction coefficient¹ of about 0.7; no attempt was made to control this variable accurately, since it affects only the intensity, not the position of the absorption bands, at least in the low range of concentration used. Similarly room temperature (approximately from 25° to 35°) was used, since the slight variation is not significant.

¹ $l^{-1} \log_{10} \left(\frac{I_0}{I} \right)$

An Abbe refractometer was used for determination of refractive indices. An average dispersion value, used in certain parts of the work, was calculated from the Amici prism settings of this instrument. Dielectric constants were taken from the International Critical Tables.

Solvents were all obtained from commercial sources. In some cases further purification was carried out; for example, all aliphatic ethers were dried with sodium; benzene was washed repeatedly with concentrated sulfuric acid until discoloration of the acid was no longer produced; anisole, o-iodotoluene, and 1-iodonaphthalene were distilled to remove discoloration. Of the solutes, the iodine, phenolphthalein, and p-rosaniline used were all commercial products. Preparation of p-nitrosodimethylaniline was carried out by direct nitrosation of dimethylaniline. Phenol blue was made by a modification of Bayrac's method (2), utilizing sodium hypochlorite in place of potassium dichromate as the oxidizing agent. It was found necessary to carry out the reaction at less than 5° C to avoid serious contamination of the product with tarry by-products which prevent recrystallization. The final product showed no evidence of impurities when chromatographed on a calcium hydroxide column with either methanol or benzene as the developer. The carotenoids, which were prepared by Dr. A. L. LeRosen, were extracted from natural sources and purified chromatographically.

In the tables on the following pages are shown the experimental results of this work. The following symbols are used:

λ_m - wave-length at absorption maximum (in millimicrons)

n_D - refractive index for the D line of the sodium spectrum, measured at about 30° C

$n_F - n_C$ - dispersion, expressed as the difference in refractive index for the F and C lines of the hydrogen spectrum (4861 and 6562 Å respectively.)

ν_m - frequency at absorption maximum (in fresnels - one fresnel is 10^{12} cycles per second.)

D - dielectric constant.

Table 1

Solute: Lycopene

Solvent	n_D	λ_m	ν_m
Carbon disulfide	1.618	479 506 545	626 593 551
1, 1, 2, 2-tetrabromoethane	1.638	- 506 541	- 593 555
Ethyl bromide	1.417	453 479 512	662 626 587
Diethyl ether	1.345	446 472 503	673 636 597
Ligroin	1.376	- 473 504	- 635 596

Table 2

Solute: Iodine

Solvent	n_D	λ_m	$n_F - n_C$	V_m
Carbon tetrachloride	1.453	520	0.0097	577
1,4-dioxane	1.417	454	0.0065	661
Hexane	1.375	525	0.0064	572
Carbon disulfide	1.618	520	0.0333	578
Benzene	1.493	504	0.0167	596
Bromobenzene	1.553	506	0.0193	593
Chloroform	1.446*	514	-	585

*Taken from handbook.

Table 3

Solute: p-Rosaniline hydrochloride

Solvent	n_D	λ_m	$n_F - n_C$	V_m
Ethylene glycol	1.4286	552	0.0097	544
Glycerol	1.4700	553	0.0082	543
Isopropyl alcohol	1.3746	551	0.0060	545
Water	1.3323	541	0.0116	555
Ethanol	1.360*	549	-	547
n-Propanol	1.385*	552	-	544
Methanol	1.331*	546	-	550
Acetic Acid	1.371*	546	-	550
Pyridine	1.5018	559	0.0161	537
Acetone	1.358*	545	-	551
Butanol	1.399*	552	-	544

*Taken from handbook.

Table 4

Solute: Phenolphthalein

Solvent	n_D	λ_m	$n_F - n_D$	ν_m
Ethylene glycol	1.4286	563	0.0069	534
Glycerol	1.4700	564	0.0082	533
Isopropyl alcohol	1.3746	568	0.0060	529
Water	1.3323	556	0.0116	540
Aqueous solutions of glucose	1.3528	556	0.0060	540
	1.3729	557	0.0056	539
Methanol	1.331*	560	-	536
Ethanol	1.360*	564	-	533
Propanol	1.385*	566	-	531
Butanol	1.399*	568	-	529
Isoamyl alcohol	1.408*	568	-	529

Table 5

Solute: p-Nitrosodimethylaniline

Solvent	n_D	λ_m	$n_F - n_D$	ν_m
Carbon tetrachloride	1.453	400	0.0097	750
Ligroin	1.376	393	0.0067	764
Benzene	1.493	411	0.0167	730
Carbon disulfide	1.618	415	0.0333	723
<u>o</u> -Iodotoluene	1.603	419	0.0234	716
Methanol	1.331*	428	-	701
Bromobenzene	1.555	418	0.0193	719

*Taken from handbook.

Table 6

Solute: Phenol blue

Solvent	λ_m	ν_m	n_D	$n_F^*n_G$	Diel. Const.
Phenyl ether	589	509	1.574	0.0218	-
Octane	550	546	1.391	0.0067	1.96
Benzene	577	520	1.493	0.0162	2.26
Ethyl ether	564	533	1.345	0.0054	4.2
1-Iodonaphthalene	607	494	1.695	0.0363	c. 5*
Acetal	588	510	1.375	0.0065	3.4
Bromocyclohexane	585	513	1.491	0.0106	-
Dioxane	571	525	1.417	0.0065	-
Pyridine	597	502	1.502	0.0161	12.2
Bromobenzene	590	509	1.553	0.0193	5.4
<u>o</u> -Iodotoluene	593	506	1.603	0.0234	c. 5*
Dodecane	557	539	1.417	0.0074	c. 2*
Heptane	549	547	1.390	0.0074	1.97
Carbon disulfide	584	514	1.618	0.0333	2.9
Cyclohexane	553	543	1.419	0.0073	2.05
Chloroform	598	501	1.446**	-	5.0
Acetic acid	610	491	1.371**	-	7.0
Butanol	606	495	1.399**	-	16.7
Isopropyl ether	567	529	1.363	0.0065	-
Butyl ether	566	530	1.393	0.0059	-
Anisole	586	512	1.509	-	-

*Estimated from values given for analogous compounds.

**Taken from handbook.

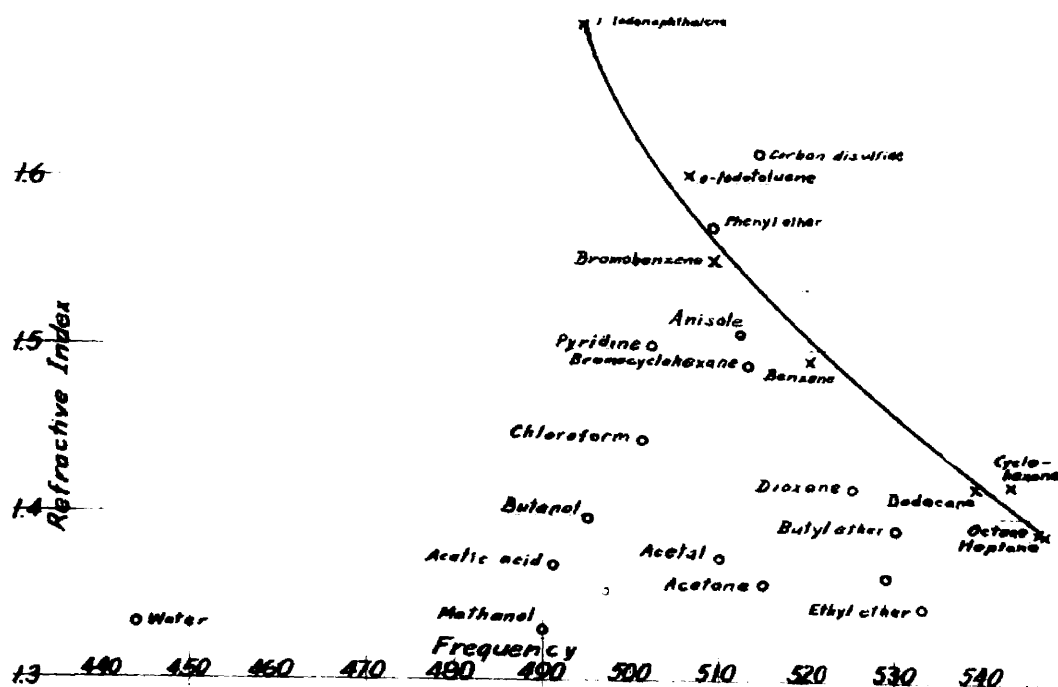


Fig. 1. Graph of frequency at absorption maximum of phenol blue versus refractive index of solvent.

x - Hydrocarbons and aryl halides

o - other solvents

(The frequency is given in fresnels. The values for acetone, water, and methanol are taken from Brooker and Sprague (5).)

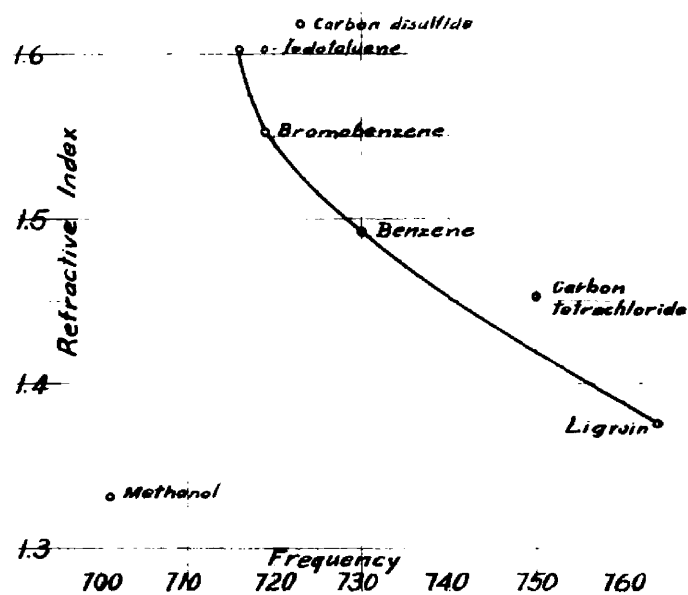


Fig. 2. Graph of frequency at absorption maximum of p-nitrosodimethylaniline versus refractive index of solvent. Note Kuhn-Brockmann effect of methanol. (The frequency is given in fresnels.)

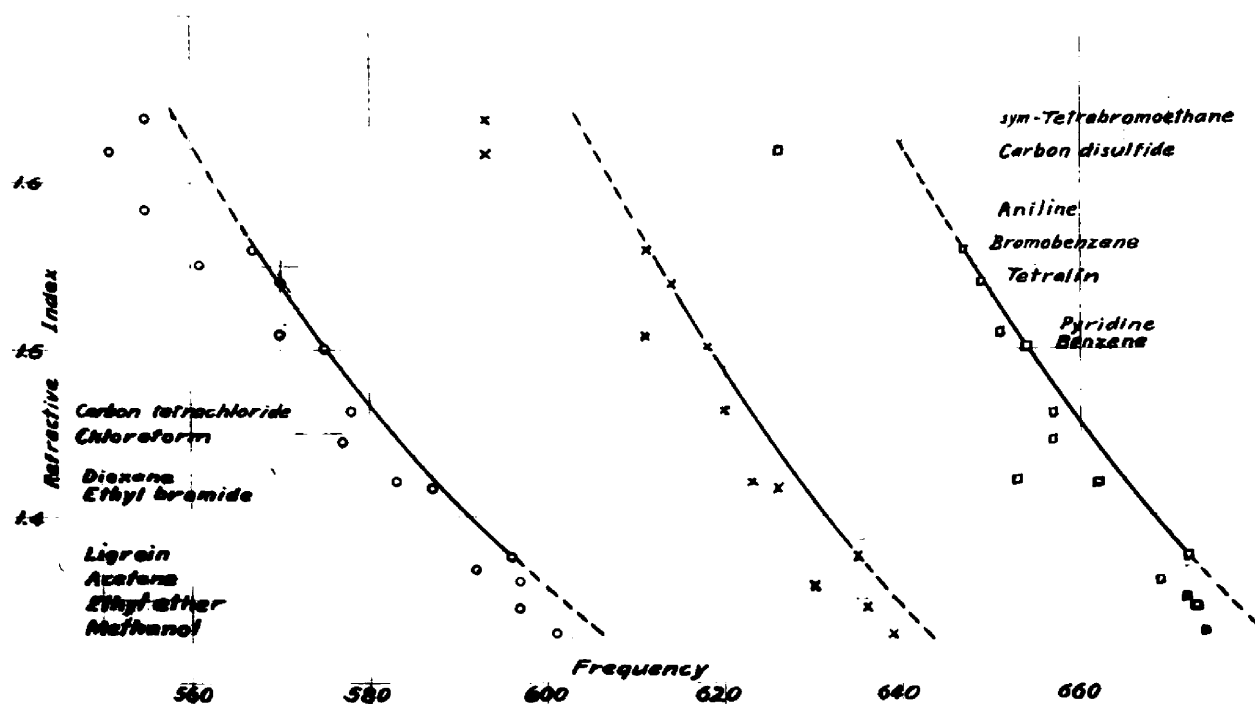


Fig. 3. Graph of the frequency at the three absorption maxima of lycopene versus the refractive index of the solvent. (The frequency is given in fresnels. Except for the data in Table 1, these data are taken from unpublished work of LeRosen carried out on a visual spectrophotometer and adjusted to account for systematic differences in the two procedures.)

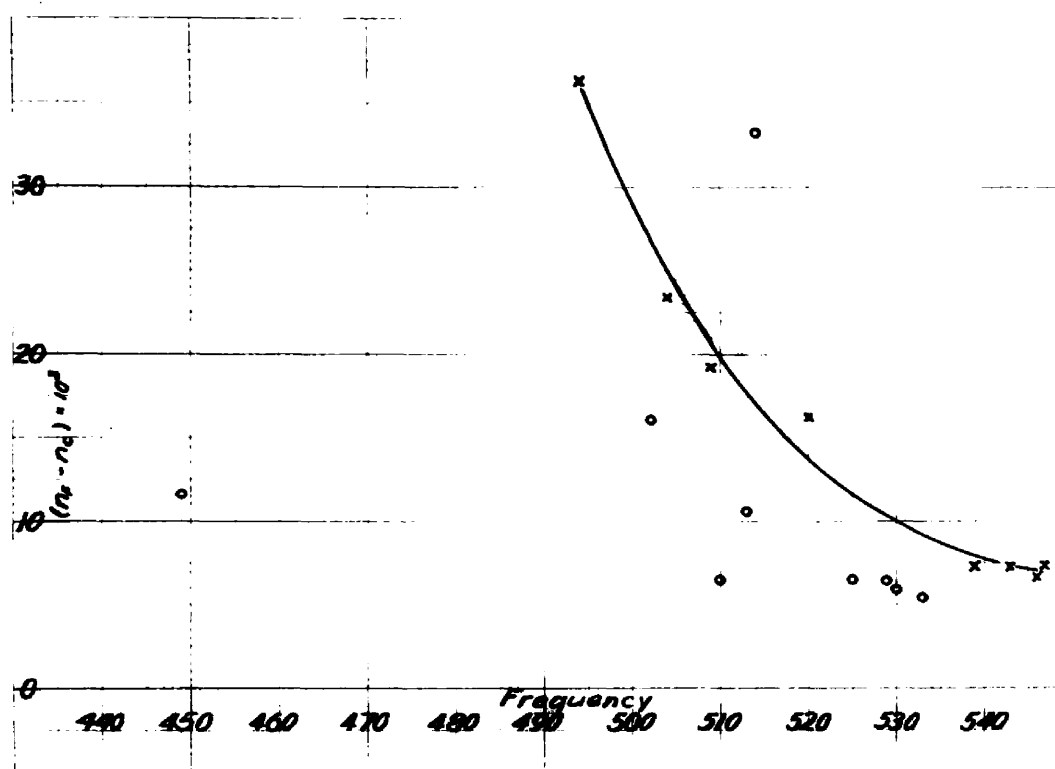


Fig. 4. Graph of frequency at absorption maximum of phenol blue versus dispersion of solvent.

x - Hydrocarbons and aryl halides

o - Other solvents

(The frequency is given in fresnels. The value for water is taken from Brooker and Sprague (5).)



Fig. 5. Graph of frequency at absorption maximum of phenol blue versus dielectric constant of solvent.

x - Hydrocarbons and aryl halides

o - Other solvents

(The frequency is given in fresnels. The values for water, methanol, and acetone are taken from Brooker and Sprague (5).)

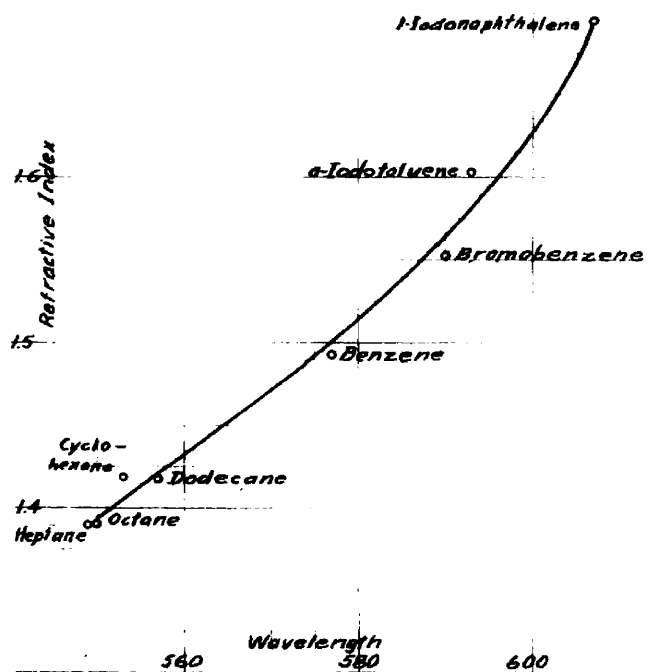


Fig. 6. Graph of wavelength at absorption maximum of phenol blue versus refractive index of solvent. (The wavelength is given in millimicrons.)

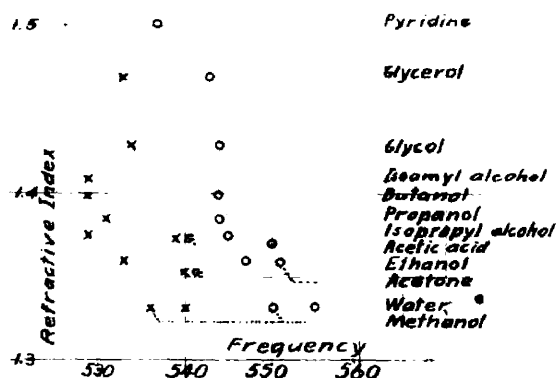


Fig. 7. Graph of frequency at absorption maximum of phenolphthalein and p-rosaniline versus refractive index of solvent.

x - Phenolphthalein

o - p-Rosaniline

(The frequency is given in fresnels. For the points marked G the solvent is an aqueous solution of glucose.)

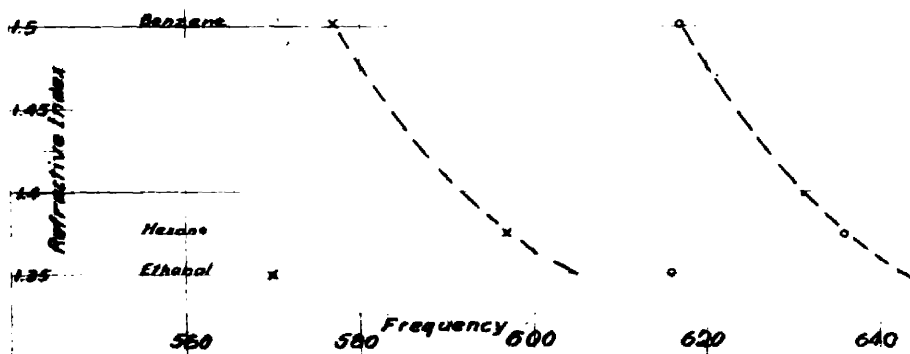


Fig. 8. Illustration of the Kuhn-Brockmann rule. Solvation by ethanol shifts the absorption maxima of the ketonic carotenoid capsanthin to about thirty fresnels less than the expected value for a non-solvating solvent. Compare effect of methanol on the carotenoid hydrocarbon lycopene (Fig. 3). (Taken from unpublished work of Ietosen.)

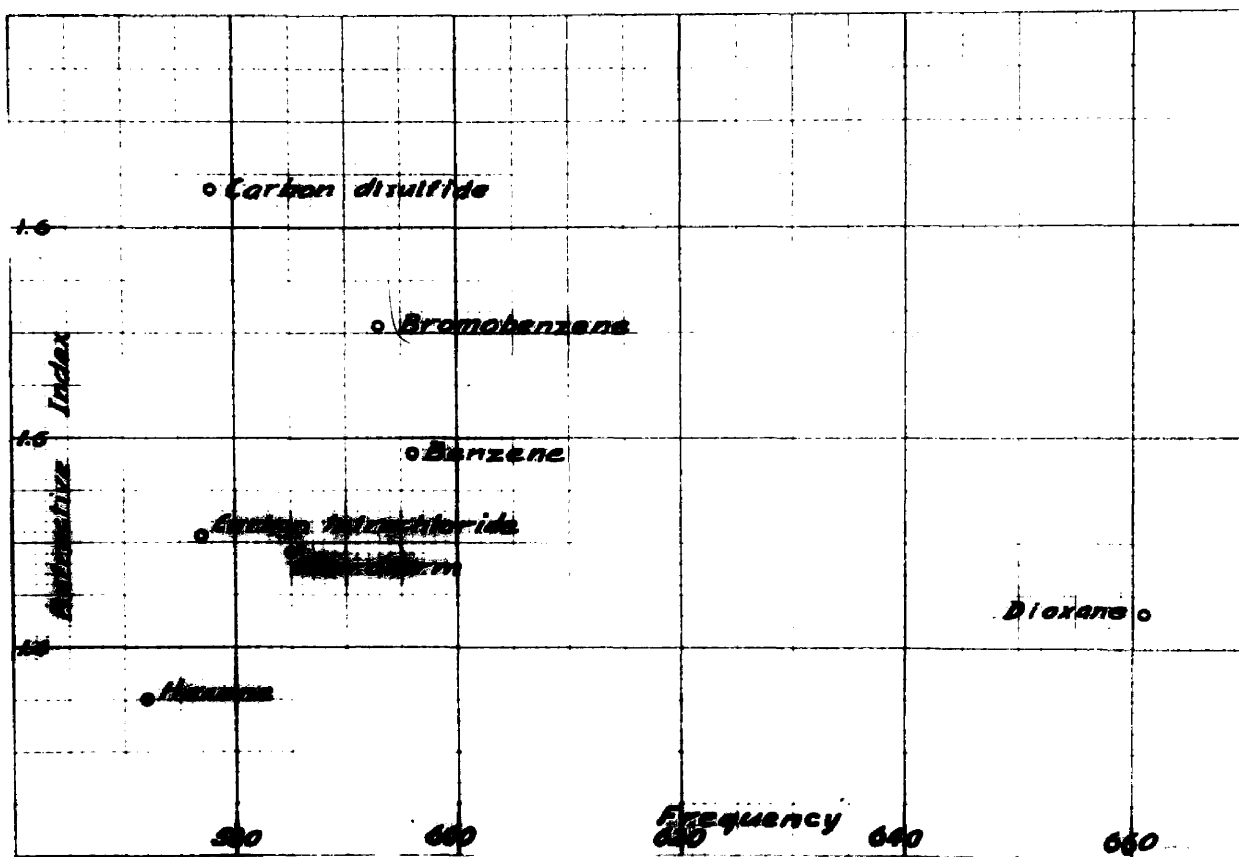


Fig. 9. Graph of frequency at absorption maximum of iodine versus refractive index of solvent. (The frequency is given in fresnels.)

DISCUSSION

1. Theories of Light Absorption, Refraction, and Dispersion

The classical theory of the interaction of light and matter (8)(10) is based on the idea that each electron in the medium, when disturbed from its rest position, oscillates about that position, the oscillations being harmonic if the medium is transparent and damped harmonic otherwise. Each electron is acted upon by a field which consists of two parts: that due to the light wave, and that due to the other displaced electrons. The development of this theory leads to the following relationships, among others:

$$I \quad n^2(1-k^2) - 1 = \sum_i \frac{\rho_i (\omega_{0i}^2 - \omega^2)}{(\omega_{0i}^2 - \omega^2)^2 + \omega_i'^2 \omega^2}$$

$$II \quad 2n^2k = \sum_i \frac{\rho_i \omega_i' \omega}{(\omega_{0i}^2 - \omega^2)^2 + \omega_i'^2 \omega^2}$$

$$III \quad n^2 - 1 = \sum_i \frac{\rho_i}{\omega_{0i}^2 - \omega^2} \quad \text{in non-absorbing regions.}$$

in which

$n \equiv$ refractive index,

$k \equiv$ extinction coefficient,

$\omega_0 \equiv$ the characteristic angular frequency of electrons
of a given type,

$\omega' \equiv$ a parameter related to the damping factor,

$\omega \equiv$ angular frequency of light,

$\rho \equiv$ a parameter dependent on density of electrons,

and the summation is to be taken over all types of electrons.

If the characteristic frequencies are far apart, then near any one of them the effect of the term containing that one will so dominate the others that the summations may be eliminated. The above equations then reduce to

$$\text{I a} \quad n^2(1 - k^2) - n_0^2 = \frac{\rho(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega'^2 \omega^2}$$

$$\text{II a} \quad 2n^2k = \frac{\rho\omega'\omega}{(\omega_0^2 - \omega^2)^2 + \omega'^2 \omega^2}$$

$$\text{III a} \quad n^2 = n_0^2 + \frac{\text{const.}}{\omega_0^2 - \omega^2} \quad \text{in non-absorbing regions.}$$

Also derived from this theory is the formula of Voigt given in the introduction.

The modern theory differs little from this in the treatment of refraction and dispersion, but absorption must be interpreted somewhat differently. According to quantum mechanics (20), a molecule or other system can

exist in any one of a number of discrete energy states. The molecule absorbs (or emits) light by passing from one such state to another, the frequency being given by the Bohr formula $\Delta E/h$ (ΔE is the difference in energy of the two states, and h is Planck's constant.) The energy of the molecule in its various states is found from the eigenvalues of the Schrödinger equation

$$\sum_i \frac{1}{m_i} \nabla_i^2 \psi + \frac{8\pi^2}{h^2} (E - V) \psi = 0$$

m_i is the mass of the i th particle (electron or nucleus).

∇_i^2 is the Laplacian operator referred to the coordinates of the i th particle.

E is the total energy of the system.

V is the potential energy of the system.

Auxiliary restraints imposed on the Schrödinger scalar ψ (that it must be everywhere finite, continuous, and single-valued) restrict the energy E to the discrete values mentioned above. (An earlier method of finding the energy levels, discovered by Heisenberg, has been shown to be mathematically equivalent to the Schrödinger method.)

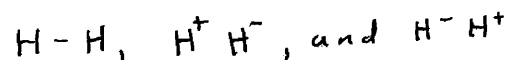
The calculation of the energy values has been carried out exactly for a few simple systems such as the hydrogen atom. For the harmonic oscillator the frequency calculated in this manner is the same as the classical frequency. The hydrogen molecule and helium atom cannot be treated

exactly, but by approximation methods accurate numerical values have been found. For more complex atoms and molecules rough approximate methods have been devised, from which in a few cases results important from a quantitative viewpoint have been obtained. Usually, however, in problems involving large organic molecules nothing more than a qualitative application of the principles of quantum mechanics is practicable; since this is true in the present work, the concepts involved will be reviewed in some detail.

In many cases approximate solutions ψ_1, ψ_2, \dots of the Schrodinger equation are available; they may have been found, for example, by neglecting some small term in the potential energy expression and solving the resulting simplified equation. Any linear combination of these, $\sum_i a_i \psi_i$, is then an approximate solution also; the energy calculated from such a combination is often lower than that calculated from any of the ψ 's alone. If the coefficients are chosen so as to minimize the energy, the resulting combination will then be a closer approximation to the true solution than any of the ψ 's; it will, in fact, be the closest approximation which the form of the function permits. This method, which is called the variation method, involves some arbitrariness from a mathematical viewpoint in that it is not theoretically necessary to introduce the functions ψ_i at all; the equation might have been solved directly without resorting first to approximations,

or a different series (for example, a Fourier series) might have been used instead of the ψ 's. However, it may make practicable calculations which would be well-nigh impossible by direct solution of the complete equation.

The above discussion serves as an introduction to the concept of resonance, which, however, can be approached in other ways also. If the ψ 's can be interpreted in terms of the physical state of the system, then the true state can be interpreted as a hybrid of the states represented by the ψ 's: the system is then said to resonate among these states. As an illustration of these ideas consider the hydrogen molecule. Functions can be set up representing the following states: (i) one electron on each nucleus; (ii) the same, but with the electrons interchanged; (iii) both electrons on one nucleus; and (iv) both electrons on the other nucleus. Resonance between the first two corresponds to a covalent bond between the atoms; the others represent ionic states. The true state is then said to resonate among the forms



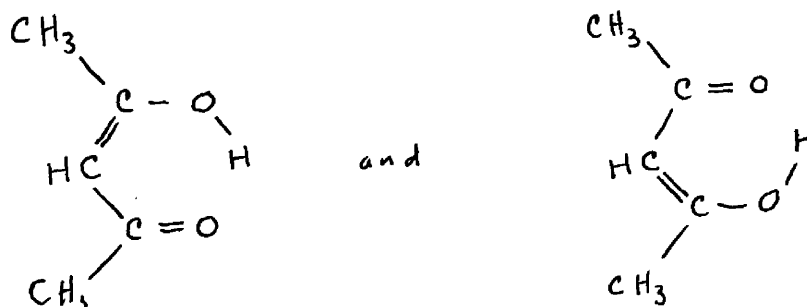
The term "resonance energy" is applied to the difference in the energy of the actual system and that of one of the states described above; the resonance energy of this system referred to two independent hydrogen atoms is responsible for the formation of a stable bond. (Accurate calculation of this energy requires the inclusion of additional ψ -func-

tions representing the polarization of each atom in the field of the other and the interaction of the electrons.)

Qualitative application of this concept to more intricate molecules has been found to require the observance of certain rules (27). The most important of these may be summarized as follows:

1. Resonance cannot occur between structures which involve appreciable differences in nuclear positions;
2. Structures of high energy make correspondingly small contributions to the actual state.

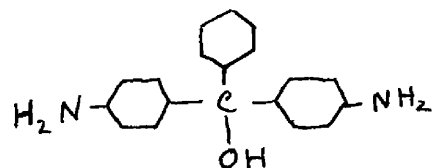
An example of the first rule is the impossibility of resonance between the keto and enol forms of acetone; in this case the two forms differ in the position of the hydrogen nucleus. However, in acetylacetone, the hydrogen atom is in the right position to complete a five-membered ring with two oxygen and two carbon atoms. Therefore the hydrogen atom can be joined to either of the oxygen atoms without appreciably changing its position, and resonance occurs between the following two forms:



Since the true state partakes of the character of both of these, the hydrogen is bound to both oxygen atoms; resonance thus clarifies the nature of the important phenomenon of hydrogen bonding (23). It was first pointed out by Bury (6) that in all colored organic compounds the structure must be represented as resonating among several conventional valence-bond structures. The importance of resonance in this case is that, when the energies are lowered sufficiently, the absorption due to change in electronic state occurs in the visible region of the spectrum, while otherwise it occurs in the ultraviolet region. An example of this effect is the contrast between the deeply colored Döbner's violet, which can resonate among such structures as the following:



and its colorless carbinol base,



in which such resonance is not possible.

2. Application of the Theories to the Experimental Results of the Present Work.

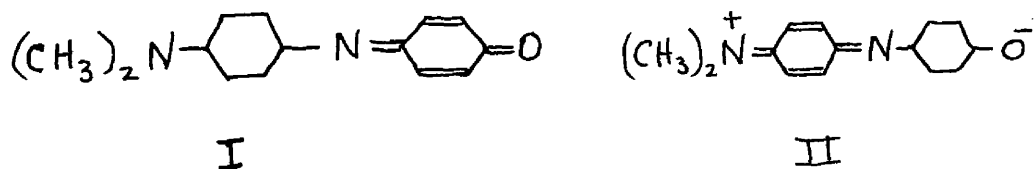
It will be seen from the graphs (Figs. 1-9) that phenol blue, p-nitrosodimethylaniline, and certain carotenoids follow Kundt's rule if the solvents are restricted to hydrocarbons and their nuclear halogen derivatives, whereas phenolphthalein, p-rosaniline, and iodine show little or no evidence of following it at all. Correlations of the position of the maximum with dispersion and with refractive index seem to work about equally well.

It is readily seen that Knoblauch's treatment, requiring proportionality of the wave-length with the refractive index does not apply even within the limitation that the solvents have no dipole moment (Fig. 6).

Direct checking of Voigt's formula requires a knowledge of such inaccessible quantities as the refractive index of the solute. This difficulty was avoided by substituting Equation IIa, Section 1, into the Voigt equation. The parameter ρ disappears on logarithmic differentiation, but ω_0 and ω' remain. These were to be found by substituting two sets of experimental values of ω and $\partial(\log n_0)/\partial\omega$ into the equation and solving the two simultaneous equations obtained for the parameters. Since the values obtained were imaginary, it was concluded that Voigt's treatment does not apply to the systems used in this investigation.

(The details of this work are given in the appendix.) Probably the reason is that the solvent affects the intramolecular constants of the solute; the absence of such influence is an essential assumption in Voigt's derivation. Since in Kundt's original work (15), as in most work on Kundt's rule, the solutes were complex organic compounds, this objection to Voigt's theory applies generally. This theory, therefore, cannot be considered the basis for Kundt's rule, although it may be valid for systems which meet the conditions that it postulates.

The results can be successfully interpreted qualitatively by modifications of the ideas of Brooker and Sprague (5). These authors found that the absorption maximum of phenol blue shifts toward greater wave-length with increasing dielectric constant of the solvent. The explanation they give is that one of the resonating forms of phenol blue is a zwitter ion (II). The high



Coulombic energy of this form makes its contribution to the normal state of the molecule small, though its contribution to the first excited state is much greater. Now if this energy is lessened by the high dielectric constant of the surrounding medium, the extent of the resonance is increased, with consequent lowering of the energy levels.

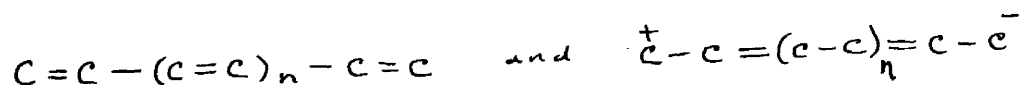
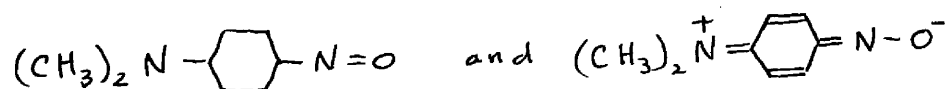
This lowering of the energy is probably greater for the excited state, since it is principally to this state that the zwitter ion form contributes. The energy difference, and accordingly the frequency of absorption, is therefore decreased.

This interpretation appears to account for the phenomena observed in Brooker and Sprague's experiment, which was confined to the four solvents cyclohexane, acetone, methanol, and water. It breaks down, however, if a wide variety of solvents is included (Fig. 5). For the hydrocarbons the shift can be correlated with dielectric constant, but correlation with refractive index succeeds equally well (as it inevitable must, since in these compounds the Maxwell relation between refractive index and dielectric constant is valid).

The dielectric constant of a fluid is due to several factors, chief of which are the electronic polarizability and the orientation of permanently dipolar molecules. It is not to be expected that in the small region near a dissolved molecule the latter is operative to the extent that it is in a macroscopic sample of the fluid; it is principally the electronic polarizability that is effective. Electronic polarization, however, is the phenomenon underlying refraction, and that part of the dielectric constant which is due to it is approximately equal to the square of the refractive index. In view of this it is to be expected

that a correlation between refractive index and position of the maximum should exist. The curvature of the graph of frequency at absorption maximum versus refractive index also receives a ready explanation on this basis - when the Coulombic attraction is sufficiently reduced, it ceases to be the controlling factor determining the extent of resonance; further reduction then has little effect on the energy. It is also to be noted that the form of the expression for Coulombic energy (with the dielectric constant appearing in the denominator) necessitates that the rate of decrease of energy with increasing dielectric constant should be lower at higher dielectric constant. The position of the absorption maximum should therefore tend toward a constant value at high refractive index, in agreement with experiment (Fig. 1).

This discussion applies equally well to p-nitrosodimethylaniline and the carotenoids (Figs. 2,3). The uncharged and zwitter ion forms of these compounds are shown below (only the chromophoric portion of the carotenoid molecule is shown).



The very large shifts shown in aqueous and methanolic solutions of phenol blue are examples of the Kuhn-Brockmann rule; solvation by hydrogen bonding is inevitable when compounds containing oxygen or nitrogen are dissolved in these solvents. Substantiation of this is found in the fact that alcohols cause large shifts with oxygen-containing carotenoids such as capsanthin and rhodoxanthin but not with carotenoids which are pure hydrocarbons, such as lycopene (Figs. 3,8). The divergences from the hydrocarbon curve shown by ethers and certain other oxygen-containing solvents and by pyridine are probably ascribable to orientation effects. It will be noted that these divergences occur with solvents having highly polarizable bonds such as carbon-oxygen or carbon-nitrogen bonds (26). If the solvent molecules tend to be oriented so that the most polarizable portions are adjacent to the solute molecule, the effective dielectric constant in the immediate neighborhood of latter molecules is increased, and the energy decreased. This decrease of energy can itself provide the driving force for the orientation. The effect must be greater if the solute contains highly polar groups such as the nitroso group. It is believed that this explanation is preferable to assuming the same type of orientation as occurs when a macroscopic field is applied, the reasons being, first, that it accounts for the fact that the effect is less with lycopene, which has no strong permanent dipoles

within the molecule, than with phenol blue, which has several such dipoles because of its carbon-oxygen and carbon-nitrogen bonds; and secondly, it shows why dioxane, with a dipole moment of zero, exhibits the effect, whereas the aryl halides, with dipole moments greater than one Debye unit, do not. Ethyl and isopropyl ethers, having small, compact molecules, should be less disturbed by thermal agitation than butyl ether, with its long chain; as expected, the divergence was found to be less when the latter is the solvent than when the lower ethers are used. Dioxane has highly polarizable bonds at each end of the molecule, and so no one portion of the molecule differs as much from the average as in the simple ethers. The effect must then be less, and the refractive index greater, than those of the corresponding simple ethers. A similar argument applies to anisole, which, because of the high polarizability of aromatic bonds (26) has a still lower shift and a still higher refractive index. In phenyl ether the effect has disappeared altogether.

On this basis the behavior of carbon disulfide remains anomalous. The abnormally large shift of carotenoid spectra in this solvent may be due to its small size, which may enable it to fill better the irregularly shaped region near the solute molecules. However, its effect on phenol blue and p-nitrosodimethylaniline is in the opposite direction. The only hint of a possible explanation which

has been found is the formation of compounds by carbon disulfide and a few complex aromatic compounds such as 6-chloro-2-methylbenzothiazole, 6-methoxy-2-methylbenzothiazole (12), and 6,13-diphenylpentacene-6,13-peroxide (1). If phenol blue and p-nitrosodimethylaniline form similar addition compounds with carbon disulfide, the effect on the spectral shift may be in either direction, since the type of bonding here is different from the hydrogen bonding on which the Kuhn-Brockmann rule is based.

with p-nitrosodimethylaniline carbon tetrachloride also gives an abnormally small shift.

Any rigorous quantitative calculation based on the concepts described above would, of course, be extremely complex. For the hydrocarbon and aryl halide solutions an attempt was made to determine whether a simple calculation of the energy of two separated charges in a dielectric medium would prove of value. This led to the equation

$$V_m = k + \frac{a}{n^2 + b},$$

k , a , and b , being experimentally determined constants. (For details see appendix.) For phenol blue the equation takes the form

$$V_m = 441 + \frac{98.9}{n^2 - 0.997}.$$

Although this equation fits the data well, the negative value of b is incompatible with the assumptions made regarding its physical significance. For this reason the equation must be regarded as empirical. It is perhaps significant that this equation obviously cannot hold for vapor spectra, since for a refractive index of unity it yields an absorption maximum in the X-ray region. Other empirical equations which fit the data reasonably well are

$$V_m = 956 - \frac{1767}{n} + \frac{1667}{n^2}$$

and

$$V_m = 459 - 208 \log_{10}(n-1).$$

Phenolphthalein and p-rosaniline are charged in all resonance forms; the forms differ in the location of the charge, but none of the principal forms involve a separation of charge. It is therefore not surprising that these compounds do not obey Kundt's rule, especially since they dissolve only in solvating solvents.

It is well known that iodine forms two types of solutions, characterized by violet and yellowish-brown colors. Piccard (21), assuming that the yellowish-brown color is due to oxygen-containing solvents, proposed that a qualitative test for oxygen in organic compounds be based on this phenomenon. However, nitrogen compounds also give a

positive test. Cennamo (7) concluded that dipole moment is the factor controlling the type of solution. This conclusion was based on the spectra of iodine in three solvents of zero dipole moment (benzene, carbon disulfide, and carbon tetrachloride) and three of non-zero moment (chloroform, methanol, and water), the former giving violet solutions and the latter yellowish-brown. Cennamo's chloroform was apparently impure, as iodine in pure chloroform yields a violet solution. Further disproof of Cennamo's conclusion can be found in the solutions of iodine in bromobenzene and dioxane. The former, with a dipole moment of 1.52 Debye units, gives a violet solution, while the latter, with a dipole moment of zero, gives a yellowish-brown solution. Kundt's rule does no better (Fig. 9). So far as any conclusion may be drawn from the present data, it appears that electronic availability is the most likely criterion for the position of the maximum in the iodine spectrum.

3. Recommendations for Further Investigations.

While the conclusion that Kundt's rule is followed only by compounds to whose structure a zwitter ion form makes appreciable contribution is followed by all compounds investigated so far, extension of the work to other types of compounds is desirable. In particular, free radicals and coordination compounds of metals should be included.

The postulate of orientation to explain the large shift exhibited by ethereal solutions of phenol blue could be

subjected to an independent test by a study of the effect of temperature variation on the position of the absorption maximum. If the orientation does occur, it must be opposed by thermal agitation, and so the effect should decrease with increasing temperature.

Since absorption bands are often resolved at low temperature into several component bands, studies at such temperatures might, by showing the effect of solvents on the individual components, reveal further points of interest.

Finally, extension of the investigation to media of higher or lower refractive index is desirable. There are not many liquids having refractive indices lying outside the range covered in the present investigation. However, a small range upward from a refractive index of unity could be covered by taking spectra on the vapor of the colored compound with or without admixture of an inert gas; if a gas having a suitable critical temperature were selected, it should be possible to extend this range almost continuously to that covered by liquids.

SUMMARY OF CONCLUSIONS

Experimentally, this work gives little ground for choice between the two forms in which Kundt's rule has been stated; refractive index and dispersion of the solvent succeed about equally well as criteria of the position of the absorption maxima of solutions of a given solute. However, the former is preferred, since it is on this basis that a reasonable physical interpretation of the results has been developed.

Kundt's rule has been found valid for systems in which the solvent is a hydrocarbon or aryl halide and the solute is a compound to whose structure a zwitter ion form makes an important contribution. If such a solute is dissolved in a solvent whose molecules have certain bonds which are more polarizable than the molecule as a whole, the maximum will appear at greater wave-length than if a hydrocarbon solvent of the same refractive index had been used. This effect is more pronounced if the solute has strongly polar bonds such as a carbon-oxygen bond than if, like lycopene, it has only carbon-carbon and carbon-hydrogen bonds. This effect appears in solvents such as alkyl halides and

ethers, for example, but not in aryl halides or diaryl ethers. A still larger shift toward greater wave-length occurs when there is hydrogen bonding between the solvent and the chromophoric portion of the solute. This is the effect first noted by Kuhn and Brockmann in solutions of rhodoxanthin.

These phenomena are believed to be due to the lessening of the Coulombic energy of the zwitter ion form by the dielectric property of the solvent. Since only the electronic polarization, not the alignment of permanent dipoles, can be effective in the small region involved, it is the electronic polarizability which is the determining factor. The close relationship of this property to refractive index accounts for the experimental correlation of the position of the absorption maximum with the latter. Molecules having certain portions which are more polarizable than others can effect a greater lowering of the Coulombic energy by so orienting themselves that these portions are nearest the solute molecule; the lowering of energy will in itself provide a driving force for such an orientation. These concepts are based on the suggestion of Brooker and Sprague that the dielectric constant of the solvent determines the position of the absorption maximum of phenol blue; in its original form, the latter idea proves untenable as soon as the behavior of phenol blue is studied in a wider variety of solvents than its authors used. All of the results of Brooker and Sprague can, however, be accounted for by the

interpretation given above.

A few anomalous results, concerned mostly with solutions in carbon disulfide, have not yet been interpreted satisfactorily.

Of ionic solutes, p-rosaniline shows little tendency to follow Kundt's rule, and phenolphthalein none at all. These compounds, in general, dissolve only in solvents which cause solvation.

Iodine spectra seem to depend on the electron availability of the solvent; no correlation exists with refractive index, dispersion, dielectric constant, density, or dipole moment.

Three empirical equations have been developed to express the dependence of the position of the absorption maximum of phenol blue of the refractive index of the solvent. These are valid for hydrocarbon and aryl halide solvents. An example is

$$\nu_m = 441 + \frac{98.9}{n^2 - 0.997}$$

(n is refractive index, ν_m frequency at absorption maximum in fresnels.)

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APPENDIX

1. Attempt to check Voigt's equation.

Voigt's equation is $\frac{\partial}{\partial \theta} \log (n_s^2 k_s) = \frac{\partial}{\partial \theta} \log n_0$. Since θ is a function of ω , the differentiation may be taken with respect to the latter variable. Equation IIa can be written in the form

$$\log (n_s^2 k_s) = \log \omega - \log [(\omega_0^2 - \omega^2)^2 + \omega'^2 \omega^2] + \log \frac{\rho \omega'}{2}$$

Differentiating this and substituting it in Voigt's equation gives

$$\frac{1}{\omega} - \frac{2(\omega_0^2 - \omega^2)(-2\omega) + 2\omega'^2 \omega}{(\omega_0^2 - \omega^2)^2 + \omega'^2 \omega^2} = \sigma$$

where $\sigma \equiv \frac{\partial}{\partial \omega} \log n_0$.

Clearing of fractions and collecting like powers of ω_0 and ω' leads to

$$a \omega_0^4 + b \omega_0^2 - \frac{b}{2} \omega'^2 - c = 0$$

in which

$$a \equiv 1 - \sigma \omega$$

$$b \equiv 2 \omega^2 (1 + \sigma \omega)$$

$$c \equiv \omega^4 (3 + \sigma \omega)$$

This may be applied to two solutions, designated by the subscripts 1 and 2. Elimination of ω' then leads to

$$\omega_0^4 = \frac{\begin{vmatrix} c_1 & c_2 \\ b_1 & b_2 \end{vmatrix}}{\begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix}}$$

or

$$\omega_0^4 = \omega_1^2 \omega_2^2 \frac{\begin{vmatrix} \omega_1^2(3+\sigma_1\omega_1) & \omega_2^2(3+\sigma_2\omega_2) \\ 1+\sigma_1\omega_1 & 1+\sigma_2\omega_2 \end{vmatrix}}{\begin{vmatrix} 1-\sigma_1\omega_1 & 1-\sigma_2\omega_2 \\ \omega_1^2(1+\sigma_1\omega_1) & \omega_2^2(1+\sigma_2\omega_2) \end{vmatrix}}$$

If $\sigma_1\omega_1 \ll 1$ and $\sigma_2\omega_2 \ll 1$, this gives $\omega_0^4 \simeq -3\omega_1^2\omega_2^2$. In the actual calculation σ_1 and σ_2 were found graphically from values of the refractive index at various wave-lengths. In every case $\sigma\omega$ was of the order of 0.05 or less, and in no case was ω_0^4 positive.

2. Attempt to derive an equation for Kundt's rule from the energy of charge separation.

If the distance between two unlike charges of magnitude e is to be increased from r_0 to r in a medium of dielectric constant D , the energy required is

$$\Delta E = \int_{r_0}^r \frac{e^2 dr}{D r^2} = \frac{e^2}{D} \left(\frac{1}{r_0} - \frac{1}{r} \right) = \frac{k'}{D}$$

If the separation involves a change in structural features

of a molecule, some additional energy c (positive or negative) may be required. If, furthermore, the effective dielectric constant of the medium around a zwitter ion is assumed to be a linear function of those of the solute and solvent, and the effective dielectric constant of the latter is identified with the square of its refractive index, the expression for the energy becomes

$$\Delta E = c + \frac{k'}{\alpha D_{\text{solute}} + \beta n^2}$$

Now if the energy difference for the ground and excited states is proportional to this, the frequency of absorption can be found as follows:

$$\nu = \frac{k'' \Delta E}{h} = \frac{k'' c}{h} + \frac{k' k''}{h(\alpha D_{\text{solute}} + \beta n^2)}$$

or

$$\nu = k + \frac{a}{n^2 + b},$$

in which $k \equiv k'' c/h$, $a \equiv k' k''/\beta h$, and $b \equiv \alpha D_{\text{solute}}/\beta h$.

AUTOBIOGRAPHY

Charles Edward Reid was born in Amite, Louisiana, on November 17, 1917, the third child of Columbus Reid and Hope Bidez Reid. His elementary education was received in the grammar school and high school of Hammond, Louisiana. After graduating in 1934, he attended Southeastern Louisiana College in Hammond for one year and then entered Tulane University. From this school he received the degree of Bachelor of Engineering in chemical engineering on June 7, 1939. From January 1, 1940, to September 15, 1945, he was employed by E. I. duPont de Nemours and Company in a tetraethyl lead plant at Baton Rouge, Louisiana. Resigning from this position, he enrolled in the graduate school of Louisiana State University. He served as a graduate assistant during the 1945-6 and 1946-7 sessions. In August, 1947, he received the degree of Master of Science in the field of chemistry. He is now a candidate for the doctorate.

On January 24, 1948, he married Miss Barbara Louise Mylius of Lake Charles, Louisiana.

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